Seleno-Aluminium Bridges.

By Professor George M. Minchin, M.A., F.R.S.

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A seleno-aluminium bridge consists of a very thin and narrow layer of conducting selenium connecting two surfaces of aluminium which are separated by an insulator, such as glass or mica. The bridge may have a linear or a circular form. If the first, it is made thus: let P and Q be two strips of aluminium separated by a very thin plate of mica SS; the whole, as we look at the figure, forms a perfectly plane surface. If the plates P, Q are connected with a galvanometer G and a battery B of a few cells, no current passes because of the insulation of the mica; but if we smear a thin layer of melted selenium over the surfaces of the plates, and, of course, over the mica, and then heat this layer in the well-known way until the selenium assumes the brownish grey modification which conducts a current, the narrow space of mica insulation is bridged over by a conductor, and the current of the battery passes.

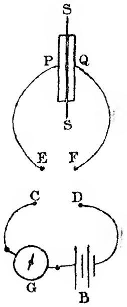

Fig. 1.

This bridge will have a certain conductivity in the dark, and that conductivity, as we shall see, will depend on the voltage of the battery B. If light—even the feeble light of a distant candle—is allowed to fall on the face of the bridge, the conductivity is very much increased, and the galvanometer will show a much increased current.

The bridge has no definite resistance (or conductivity) because it is different for different voltages of the applied battery, and, of course, much depends on the extent of the surface of the mica separator; but, roughly speaking, it will be in the neighbourhood of 40 or 50 megohms if the length of the plates P, Q is about a centimetre and the thickness of the mica about 0·01 mm. The galvanometer G should be a sensitive D'Arsonval dead-beat one.

The circular form is made by boring a cylindrical hole through a thick rod of aluminium, placing in this hole a tightly-fitting thin glass tube, and forcing into this glass tube a tightly-fitting rod or wire of aluminium. The surfaces of aluminium tube, glass tube, and aluminium wire are worked quite plane, and selenium is then (as above) smeared over them so as to bridge across the glass separator. Thus the outer aluminium tube and the inner aluminium rod or wire take the places of the two plates P, Q in the above figure. If the diameter of the glass tube is about 0·5 mm., the image of a star can be focussed on the little ring, or bridge, of selenium, and the light of the star will alter the conductivity of the bridge and give an increased deflection on the galvanometer scale.

If the linear bridge is used, we can place the thin line SS of the bridge in any part of the spectrum of the star and obtain the deflections caused by lights of various colours or wave-lengths.

As indicated in the figure, one pole of B is always connected with a fixed pole of the galvanometer, while the poles E and F of the bridge can be connected, respectively, either with C and D (the second poles of the galvanometer and battery) or with D and C. It is thus seen that the battery current always passes through the galvanometer in the same sense, but that the sense in which it passes through the bridge can be varied.

Before we answer the question: how does the change of conductivity of the bridge (or the deflection on the galvanometer scale) depend on the intensity and the colour of the incident light? we must find how the employment of different voltages in the battery B affects the results. To determine this, I connected the bridge successively with batteries of 2, 4, 6, 8, 10, and 12 volts, and the following are the numbers representing the corresponding current strengths indicated by the galvanometer: 35, 104, 203, 367, 558, 793. Each of these currents took a considerable time to establish itself—roughly from 20 minutes to half an hour. The effect is a gradual one. Dividing the currents by the corresponding voltages, we have for the corresponding conductivities the numbers: 17·5, 26, 36, 46, 56, 66. Thus *the conductivity is not constant, but is a function of the voltage.*

The accompanying figure (fig. 2) represents as ordinates the currents and the conductivities corresponding to the voltages.

The curve at the left of the figure is the diagram of current-strengths produced, when the bridge is in the dark, by different voltages, while that at the right represents the corresponding conductivities of the bridge, and we may, I think, accept this latter as a right line. Thus, if V is any voltage and c the corresponding conductivity,

$$c = k\mathrm{V} + \mathrm{K}, \tag{1}$$

where K is the conductivity, represented by the ordinate of the point A, when an infinitely small voltage is applied. This K can be regarded as the *intrinsic conductivity* of the selenium. If C_0 denotes the final current produced by any voltage V, the curve at the left is a parabola, since $\mathrm{C}_0 = c\mathrm{V}$, or

$$\mathrm{C}_0 = \mathrm{V}(k\mathrm{V} + \mathrm{K}), \tag{2}$$

which denotes a parabola whose vertex is at the left of the axis of current and below the axis of voltage.

To determine the law of variation of current with the intensity of light, I used the spectrum of a Nernst lamp, placing the bridge at distances 6, 5, 4, 3, 2, and 1 metres from the source, the bridge being slid up the inside of a very thick cylinder of cardboard blackened on the inside; but this was not found to be a very convenient arrangement, so I finally confined the observations to two coloured lights—one a pure red, and the other a very nearly pure blue. These lights were produced by passing the light of the Nernst lamp through solutions of fuchsine in water and sulphate of copper in ammonia.

If R_0 is the resistance of the bridge in the dark for a given voltage, and R its resistance when light of intensity i falls on it, the fraction $(R_0-R)/R_0$ suggests itself as a quantity whose connection with i might be determined; but there is no very simple function of i which measures this quantity. After many trials, I found the following to be a relation which is very fairly accurate :—

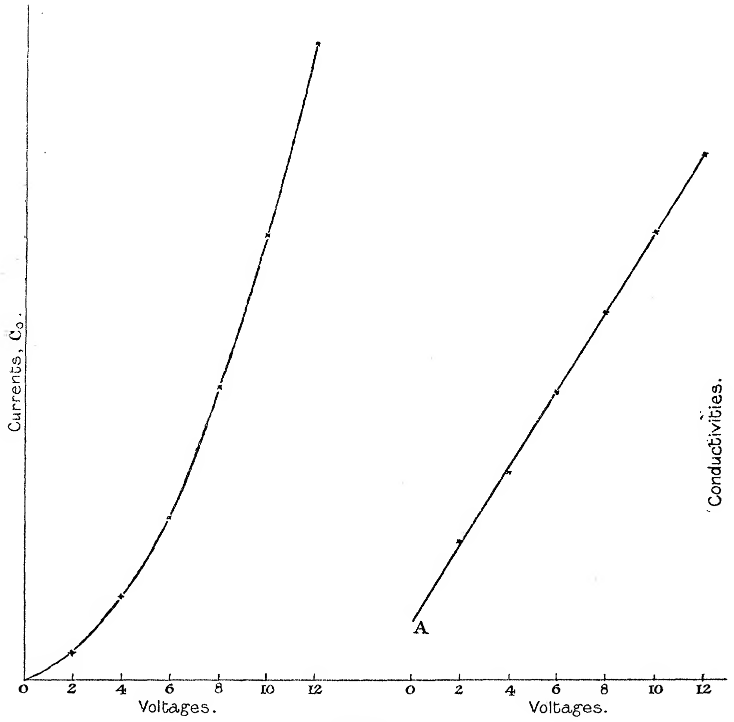

Fig. 2.

Let i_1 be the intensity of light of a given wave-length, which alters the current C_0 into C_1, and i the intensity of the same light, which alters C_0 into C ; then

$$\log\frac{C}{C_0} = \left(\frac{i}{i_1}\right)^n . \log\frac{C_1}{C_0}, \tag{3}$$

It does not matter what the voltage of the auxiliary battery B is, the ratio C/C_0 is practically the same. Of course, the C_0 corresponding to a voltage of 6 is much greater than the C_0 corresponding to a voltage of 2, but so is the C produced by a given light greater with the first voltage than with the second.

The light of the Nernst lamp was made to pass through a rectangular glass trough filled with water, so that the heat rays might be cut off; from this trough it passed through a thin glass trough containing the coloured liquid; and thence it was passed through a series of thick cardboard cylinders, each 1 metre long and 1 decimetre in diameter. These cylinders were blackened on the inside and placed end to end, so that we could use a cylindrical tube varying in length from 1 metre to 6 metres. The selenium bridge was placed at one end of this tube, and was, of course, completely screened from all light, except that of the Nernst lamp.

The focus from which the central rays of the incident light could be considered to emanate was about 14 cm. from the end of the tube, so that the distances of the luminous point from the bridge, with successive lengths of tube, were approximately 1·14, 2·14, 3·14, 4·14, 5·14, and 6·14 metres.

The following table shows the values obtained for C/C_0 at the various distances employed for the red and blue lights, the battery employed with the first having a voltage of 2, and with the second a voltage of 4:—

Distances......	6·14.	4·14.	3·14.	2·14.	1·14.	
C/C_0, red	1·83	2·13	2·33	2·83	4·27	2 volts.
C/C_0, blue	1·205	—	1·355	1·484	1·875	4 volts.

Applying equation (3) to red light at distances 6·14 and 1·14, we have

$$\log 1{\cdot}83 = \left(\frac{114}{614}\right)^{2n} . \log 4{\cdot}27,$$

since the intensities are inversely as the squares of the distances. This gives $n = 0{\cdot}262$. Similarly for the other distances employed, and the values of n which we find are successively

0·262, 0·253, 0·266, 0·264.

For the blue the values are

0·361, 0·359, 0·369.

The mean value for the red may be taken as 0·26, and that for the blue 0·36.

The accompanying figure shows two curves whose ordinates are the values of C/C_0 for the red and blue, the abscissæ being the intensities of the light.

The larger the voltage of the auxiliary battery B, the larger will be the values of C; but the value of C/C_0 for a given intensity and colour is found to be the same whatever the voltage.

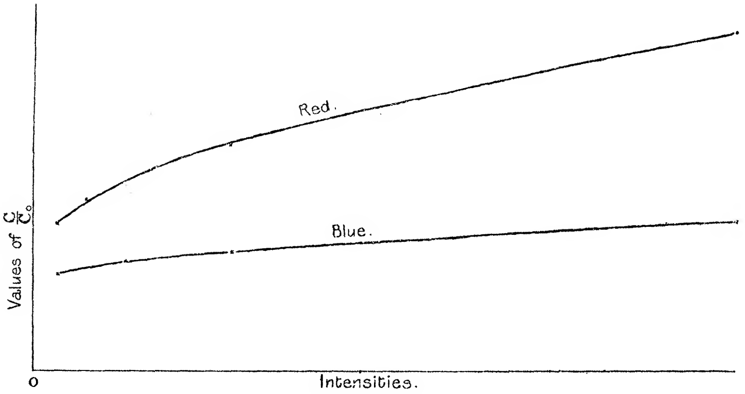

Fig. 3.

The red light belonged to that part of the spectrum in the neighbourhood of the ray B, and the blue to the portion about midway between F and G. If we take the ratio of the wave-lengths in these parts of the spectrum as roughly equal to 64 : 41 and compare this with the ratio of the index n in equation (3) for the blue to the value of n for the red—namely 36 : 26—we find the two ratios not very different. This suggests that n is inversely proportional to the wave-length, and that equation (3) may be written in the form

$$\log\frac{C}{C_0} = \left(\frac{i}{i_1}\right)^{k/\lambda} . \log\frac{C_1}{C_0}, \tag{4}$$

where k is a constant depending merely on the selenium bridge employed.

In constructing these bridges I have found it desirable to coat the selenium layer with a very thin layer of melted paraffin. A small piece of paraffin laid on the face of the bridge while it is yet hot is spread over the selenium with a hot glass rod. This paraffin gives the surface of the grey layer of selenium a blackish appearance, but does not in the least diminish its sensitiveness to light. It is just possible that it rather increases the sensitiveness. At any rate, it protects the selenium from the action of vapour in the air, and it seems to facilitate the return of the bridge to its natural state when the light is withdrawn.

I must now mention a very strange peculiarity of the bridge, of which

I have no explanation. It is that after exposure to light *its resistance to a current traversing it in one direction is not the same as to a current traversing it in the opposite direction.* The difference in the resistances to currents flowing through the bridge in opposite directions was sometimes found to amount to more than 30 per cent. with a voltage of 6. This would seem to imply a residual electromotive force in the bridge after the light is withdrawn, so that the bridge becomes a "cell," and not a mere resistance; but this is not so: when we seek for a deflection due to the bridge alone (by cutting off the battery), we find no deflection whatever.

Also, when the light is withdrawn the return of the bridge to its natural state (or of the spot on the scale to its initial position) is very much accelerated by reversing the current through the bridge several times and then breaking the circuit.

Two of the facts which I have given above—namely, that the resistance of selenium to a current is not independent of the voltage of the battery employed, and that its resistance is not the same to two currents traversing it in opposite directions—were new to me when I observed them in the course of these experiments; but Dr. Shelford Bidwell pointed out to me that both facts were discovered previously by Adams and Day. Their paper on selenium "cells" (more properly *resistances*) is in the 'Phil. Trans.' for 1877; and, on examining it, I find some observations which do not agree with what I have found for seleno-aluminium bridges. Adams and Day used a thin plate of crystalline selenium 5·4 cm. long, 1·2 broad, and 0·08 thick, with platinum wires fixed into it and its ends.

I always use aluminium and not platinum, because when working with selenium *cells* (in which a voltage is generated) I found much greater sensitiveness with aluminium than with platinum.

Adams and Day found that when this plate was inserted in the circuit of a battery and galvanometer, as in fig. 1 above, the longer the current was allowed to flow the *greater* became the resistance of the selenium. This is precisely the reverse of what I have observed, and it seems to point to some chemical action at the electrodes.

Owing to this, they never allowed the current of the battery to pass through the plate for more than 15 seconds, so that they could not have obtained the result given in equation (1) above; for the *final* value of the conductivity of a bridge is attained after a time very much greater than 15 seconds.

Another notable difference in the results is this: Adams and Day, using exposures of 10 seconds, found that the change of resistance produced by light "varies exactly as the square root of the illuminating power." For a considerable time I believed, from observation, that the *fourth root* of the intensity was nearest to the truth; but I found that no such law agreed satisfactorily with experience. If δ is the amount by which a resistance R_0 (in the dark) is diminished by light of a given colour and intensity i, equation (3) above gives

$$\delta = R_0(1 - e^{-ki^n}), \quad (5)$$

where k is a constant, and n is a number depending on the colour of the light. This equation does not make δ proportional to $\sqrt{i}$.

If i is comparatively feeble, and therefore δ small compared with R_0, this equation makes δ/R_0 proportional to ki^n; and since n is not very different from $\frac{1}{4}$ for red light, the change of resistance is roughly proportional to the fourth root of the intensity.

A peculiarity of my seleno-aluminium bridges which must be mentioned is this: after the bridge has been in use for a considerable time (perhaps some months) its resistance for high voltages is extremely unsteady. Thus, a bridge which had been much used had a perfectly steady behaviour with 2 volts, but with 6 volts the spot on the scale moved with great suddenness over large distances, the bridge being all the time in the dark.

The Time-current Curve.

A very important question relates to the *time-current curve, i.e.*, the curve whose ordinates represent the values of the current at different times during the exposure to light, the abscissæ being the corresponding times.

The following typical figures represent a time-current curve for red light and one for blue (fig. 4, p. 16).

The observations of the deflections on the scale were made at intervals of 15 seconds, and the values of the time, t, as multiples of this interval, are set off along the axis OT, while the values of the current are measured along OY. The points A, *b*, C, D . . . H represent the observations with red light, the voltage of the auxiliary battery being 4, and the distance of the radiant point of the light of the Nernst lamp from the bridge 2·14 metres (called roughly 2 metres in the diagram). The curve A′, B′, C′ . . . similarly represents the results with blue light. Two different selenium bridges were used in these observations, and OA represents C_0, the current in the dark, in the first case, while OA′ represents the C_0 in the second case.

If the two bridges employed had been the same, the points A and A′ would be the same; but they are sufficiently close to show the difference between the curves.

With red light at such a small distance as 2 metres the rise of the current at the instant of exposure of the bridge to the light is so rapid that no trust-

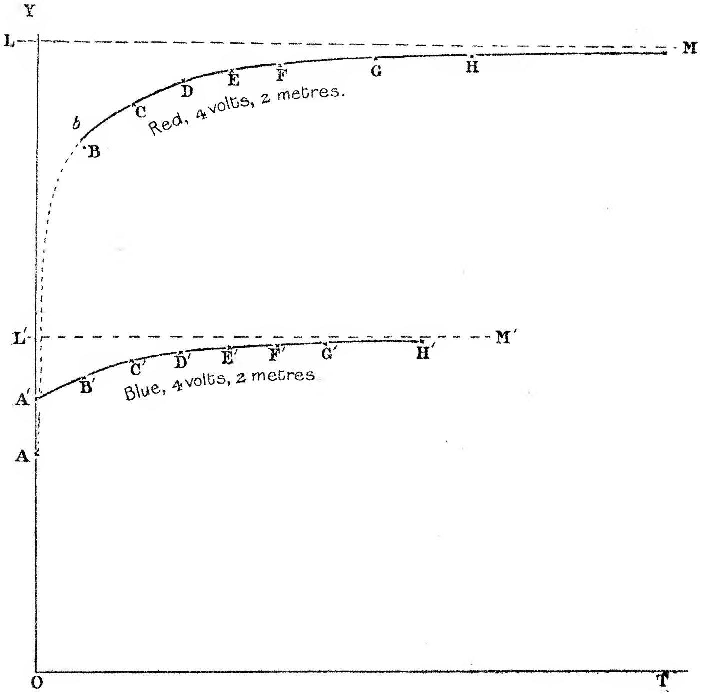

Fig. 4.

worthy observation of the deflection during the first 15 seconds—even with a D'Arsonval galvanometer, which is said to be "dead-beat"—can be made: the needle is too rapidly on the move, and even if its deflections were photographed, we could scarcely infer the current-strength from them, owing to inertia.

Hence the position of the point *b*, which represents an attempt at a reading at the end of the first 15 seconds, is quite untrustworthy.

Representing the interval of 15 seconds by τ, and the current by C, the following were the actual readings with the red:—

t.	0.	τ.	2τ.	3τ.	4τ.	5τ.	7τ.	9τ.	13τ.	∞.
C......	54	130	141	147	149·8	151	153	154	155·3	156

(ρ)

the fractions of divisions being rough estimates.

For the blue the corresponding table is—

t.	0.	τ.	2τ.	3τ.	4τ.	5τ.	6τ.	8τ.	∞.
C ……	68	73	77	79	80·1	81	81·3	82	83

(β)

Both the voltage and the distance of the light from the bridge were varied in other experiments.

In the absence of a knowledge of the physical cause of the action of light on selenium, it is allowable to make a hypothesis which will accord with these observations and the curves representing them; and I therefore make the following plausible assumption:—

If C is the current-strength at any time t after exposure, and H the final value attained by C—represented by the height of the line LM in fig. 4 for red light—the time-rate of increase of C, viz., dC/dt, should be proportional to $H-C$, or to some power of $H-C$; that is, we assume that

$$dC/dt = k(H-C)^p, \tag{6}$$

which gives

$$(H-C)^{-m}-(H-C_0)^{-m} = \lambda t, \tag{7}$$

where we use m for $p-1$ and λ for $k(p-1)$.

The quantities to be determined in this equation are H, m, and λ; and they can be theoretically found from three simultaneous values of C and t.

To see how such an equation satisfies the results, take the table (ρ); discard the reading for $t = \tau$, since it is known to be untrustworthy, and take C_2 and C_3, *i.e.*, the values of C corresponding to 2τ and 3τ, at the same time using our knowledge that $H = 156$. We have then the equations

$$15^{-m}-102^{-m} = 2\lambda\tau, \tag{8}$$

$$9^{-m}-102^{-m} = 3\lambda\tau, \tag{9}$$

which give for m the equation

$$3(15)^{-m}-2(9)^{-m}-(102)^{-m} = 0. \tag{10}$$

Of course, one value of m is 0—a point to which we shall revert presently; but there is another, and it is at once located between $\frac{1}{2}$ and 1 with no trouble; and then by trial we find that $m = 0{\cdot}554$, giving $\lambda = 0{\cdot}07297/\tau$, will almost exactly satisfy the equations (8) and (9).

Assuming these values, (7) becomes

$$(H-C)^{-0{\cdot}554} = 0{\cdot}07713+0{\cdot}07297t/\lambda, \tag{11}$$

where $H = 156$. If by means of this we *calculate* the values of C_1, C_4, C_5, we find 125·3, 149·9, 151·6, while the observed values are 130, 149·8, 151;

and these confirm the statement that the first observation was untrustworthy.

Treating the table (β) in the same way, the equations to be solved are—

$$6^{-m} - 15^{-m} = 2\lambda\tau,$$

$$4^{-m} - 15^{-m} = 3\lambda\tau,$$

which give

$$3\,(6)^{-m} - 2\,(4)^{-m} - (15)^{-m},$$

from which we find $m = 0{\cdot}184$ and $\lambda = 0{\cdot}0558/\tau$, and therefore

$$(\mathrm{H}-\mathrm{C})^{-0{\cdot}184} = 0{\cdot}6076 + 0{\cdot}0558t/\tau, \tag{12}$$

where $\mathrm{H} = 83$. If from this we calculate the value of C_1, we find $\mathrm{C}_1 = 73{\cdot}7$, while the observed value is 73—a not very different value. This result is to be expected, because with blue light the motion of the spot on the scale is slow enough to allow of an observation at the end of the first 15 seconds.

The curve represented by equation (7), and shown in fig. 4, has an asymptote parallel to OY at a distance $\{\lambda\,(\mathrm{H}-\mathrm{C}_0)^m\}^{-1}$ from OY to the left; and if this asymptote and LM are taken as axes of y and x respectively, the equation of the curve is

$$y = \lambda^{-1/m} \, . \, x^{-1/m}.$$

For the particular curves (11) and (12), for red and blue, represented in the figure, the distances of the second asymptote from OY are about $1{\cdot}6 \times \tau$ and $10{\cdot}9 \times \tau$, respectively.

The importance of a knowledge of the time-current curve is obvious in connection with the measurement of starlight with a selenium bridge, because if we know the nature of the curve, the final value H of the current due to a star's light can be inferred from two or three observations immediately after exposure, without the necessity for, perhaps, a long delay until the current attains its maximum; in that case the exposure to the light of a given star can be very short. The quantity H can be found, together with m and λ, from three equations of the form (7) by making $t = \tau$, 2τ, 3τ successively.

That a value of m, distinct from zero, satisfying two equations of the forms (8) and (9) can always be found appears thus—

Suppose that $\mathrm{H}-\mathrm{C}_0$ is equal to c, and that $\mathrm{H}-\mathrm{C}$ is a when $t = p\tau$, and $\mathrm{H}-\mathrm{C} = b$ when $t = q\tau$, where $p < q$, and therefore $a > b$; then

$$q\,(a^{-m} - c^{-m}) - p\,(b^{-m} - c^{-m}) = 0.$$

Now c is, of course, $> a$ and $> b$; and the left side of this equation is

$$q\,\{(c/a)^m - 1\} - p\,\{(c/b)^m - 1\},$$

which for some value of m must vanish, because $(c/a)^m < (c/b)^m$ for positive values of m, so that the multiplier of q in this expression is less than that of p, while $q > p$, and the ratio of the second coefficient to the first increases indefinitely with m.

The values of the constants m and λ depend in some unknown way on the voltage and on the intensity of the light.

When H is found, the intensity of the light is known from equation (3) into which H is to be put for C, i_1 being the intensity of some standard light which produces a final current C_1.

Effects in the Spectrum.

Adams and Day found that " the effect was greatest in the greenish yellow and in the red of the solar spectrum, the violet and ultra-red rays producing very little, if any, effect." My observations with a seleno-aluminium bridge are not in complete agreement with this. Passing the light of a Nernst lamp through a quartz lens, in the focus of which the face of the lamp was placed, receiving the parallel emergent beam on a quartz prism, and finally focussing, by means of another quartz lens, the various parts of the spectrum on the end of the long cardboard cylinder employed in these experiments, I examined the effects produced by the rays in, and beyond both extremities of, the spectrum. The end of the cardboard tube on which the spectrum was focussed was closed by a cap in which a slit could be opened; the selenium bridge was placed at the middle of the other end of the tube, 6 metres distant from the slit, and a battery of 2 volts was used. I found a very marked effect produced by rays a long way below the red, and a considerable effect produced by the violet.

The following figure represents roughly the results obtained:

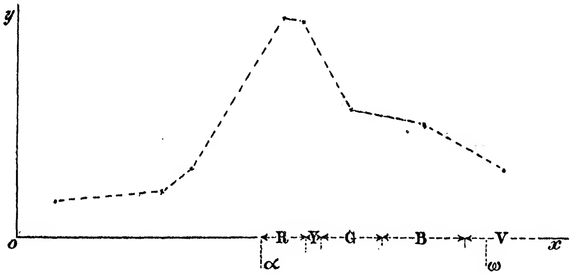

FIG. 5.

The visible spectrum of the lamp is represented in length by $\alpha\omega$, and its coloured bands by the letters R, Y, G, B. The yellow Y was a very narrow band, not very well marked, and the violet V was somewhat indefinitely marked beyond the blue.

The ordinates represent the values of δ/R_0, where R_0 is the resistance of the bridge in the dark and δ the change of resistance produced by the radiation received by the bridge. The maximum is in the red, and it amounted to 0·58. The ordinates corresponding to the angular points of the diagram, counting from 0 towards x, represent the values

0·09, 0·12, 0·18, 0·58, 0·57, 0·34, 0·30, 0·18.

It appears from this that there is a very considerable effect produced by infra-red radiation.

The Use of Narrow Bridges.

The purpose for which an almost infinitely narrow bridge of selenium was constructed is to measure the strength of the radiation in various parts of the spectrum of a star by comparing the effect with that of a standard light of the same colour, or the light in the same part of the spectrum of another star.

From the results obtained with red and with blue, it seems that there is little use in exposing a selenium surface to the total light of a star or a planet, as has been hitherto done; for the effects produced by different coloured lights follow different laws as to intensity.

Hence it seems that the most proper course is to use the spectrum of the star, and to expose the selenium to different bands in this spectrum. This I propose to do shortly, on the invitation of Dr. A. A. Rambaut, at the Radcliffe Observatory. The experiments detailed in this paper, made (and still in process) at the Electrical Laboratory, Oxford, were necessary as a preliminary to the stellar work, because it is clearly essential that we should know how to connect the observed effect on the bridge with the intensity of the light producing it, and to ascertain whether the different components of a compound light follow the same law or not. A scarcely less important object is the discovery (even though only approximate) of the nature of the time-current curve.

The experiments of Adams and Day were made with large surfaces of selenium, so that a part of the surface could be exposed to light while the rest was in the dark; and a large part of their work relates to the residual effects (or polarisation currents) produced from the selenium to its electrode when the light is withdrawn. My observation that no such effects are produced in a very narrow seleno-aluminium bridge does not contradict their observations, because the bridge is so narrow that the whole of it must be exposed at once.

Finally, it is necessary to point out the difference between seleno-aluminium *bridges* and the seleno-aluminium *cells* which I used some years ago. The latter are true "cells," containing a liquid and two metallic surfaces, and they generate a voltage by exposure to light: the former are *resistances* simply; but they will probably prove much more convenient, because they are used with a galvanometer instead of an electrometer.

On the Theory of Capillarity.

By E. T. Whittaker, Sc.D., F.R.S.

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§ 1. The fundamental quantities in the theory of capillary phenomena are the *surface-tension* γ (which we shall suppose expressed in dynes per centimetre), and the *surface-energy* λ (which we shall suppose expressed in ergs per square centimetre). The relation between these two quantities is at once given by the thermodynamic equation connecting available energy with total energy: it is therefore

$$\gamma = \lambda + \mathrm{T}\frac{d\gamma}{d\mathrm{T}}, \tag{1}$$

where T denotes absolute temperature.

This equation implies that when the area of a surface of separation is increased by 1 cm.^{2} at temperature T, the external agencies do work amounting to γ ergs against the surface-tension: and this energy, together with a further contribution of $-\mathrm{T}d\gamma/d\mathrm{T}$ ergs which is appropriated from the heat-energy of neighbouring bodies, becomes resident in the film, giving rise to an increase of λ ergs in its internal energy.

The relation between the surface-tension and surface-energy is, of course, exactly the same as the relation between the electromotive force of a voltaic cell and the energy of the chemical reactions which occur in the cell.

§ 2. As in the comparative theory of chemical substances the heat evolved by a reaction is a more fundamental quantity than the E.M.F. of a cell which can be based on the reaction, so in molecular theory the internal energy of a surface of separation is a more fundamental quantity than the surface-tension to which it gives rise; and it therefore becomes of importance to study the above quantity λ.

Now the value of the surface-tension γ has been experimentally determined for several liquids over wide ranges of temperature by Ramsay and Shields;[*] from their results it is possible by the equation (1) above to

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[*] 'Phil. Trans.,' A, vol. 184, 1893, p. 647.